



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C07C</b>	<b>A2</b>	(11) International Publication Number: <b>WO 97/03034</b> (43) International Publication Date: 30 January 1997 (30.01.97)
<p>(21) International Application Number: PCT/US96/11499</p> <p>(22) International Filing Date: 10 July 1996 (10.07.96)</p> <p>(30) Priority Data: 60/001,018 10 July 1995 (10.07.95) US</p> <p>(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).</p> <p>(72) Inventors: LYSENKO, Zenon; 214 West Meadowbrook Drive, Midland, MI 48640 (US). WESSLING, Ritchie, A.; 1608 West Saint Andrews Road, Midland, MI 48640 (US). PICKELMAN, Dale, M.; 319 Price, Auburn, MI 48611 (US). ROSE, Gene, D.; 216 East Saint Andrews Road, Midland, MI 48642 (US). LADIK, Mladen; 4714 Blossom Circle, Midland, MI 48642 (US). KRAYUSHKIN, Michael; Building 2, Apartment 44, Kosinskaya Street 20/11, Moscow, 111538 (RU).</p> <p>(74) Agent: WILLIS, Reid, S.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).</p>	<p>(81) Designated States: AU, BR, CA, CN, FI, HU, JP, KR, MX, NO, PL, RU, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i></p>	
<p>(54) Title: POLYNITRILE OXIDES</p>		
<p>(57) Abstract</p> <p>The present invention is an aqueous dispersion of a stable polynitrile oxide represented by the structure: <math>R-(C\equiv N-O)_x</math>, where x is an integer greater than 1, R is an aromatic, aliphatic, or cycloaliphatic group having at least one substituent adjacent to each nitrile oxide group, the substituent characterized by inhibiting dimerization of nitrile oxide, and being non-interfering with a reaction between nitrile oxide groups and unsaturated groups. The present invention is also a method of curing a latex having a polyunsaturated disperse phase, comprising the steps of: a) mixing the latex with a stable polynitrile oxide; and b) removing water from the mixture. The present invention provides a simple means of preparing one-part coating systems that can be cured at room temperature without the release of by-products.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## POLYNITRILE OXIDES

The present invention relates to stable polynitrile oxides.

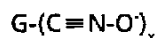
Nitrile oxides react with unsaturated compounds to form cyclic compounds. For example, nitrile oxides react with a) olefins and alkynes to form isoxazolines and isoxazoles, respectively; b) aldehydes and ketones to form 1,3,4-dioxazoles; c) thiocarbonyls to form thiooxazoles; d) imino compounds to form 1,2,4-oxadiazolines; e) isocyanates to form 1,2,4-oxadiazolinones; and f) carboxyls to form hydroximic acids. (See Grundmann and Grunanger, Nitrile Oxides, Springer, New York, pp. 85-139, 1971.)

Nitrile oxides can be prepared by a number of methods, most notably from the dehydrohalogenation of the corresponding hydroximic acid halide, which can be prepared by the halogenation of the corresponding aldoxime. The aldoxime, in turn, can be prepared by reacting the corresponding aldehyde with a hydroxyl amine. General methods that teach the preparation of nitrile oxides are described in Nitrile Oxides, *supra*, pp. 31-61.

Because nitrile oxides tend to dimerize in the absence of stabilizing groups, it is desirable to either prepare the nitrile oxides *in situ*, or to prepare stabilized nitrile oxides. Nitrile oxides can be stabilized by the presence of substituents, such as ethyl, methyl, methoxy, or methylsulfide groups adjacent to the nitrile oxide group (see Nitrile Oxides, *supra*, p. 14). Examples of stable nitrile oxides, including stable bis-nitrile oxides are disclosed in Nitrile Oxides, *supra*, pp. 16-21; Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, pp. 1201-1203 (1991); and Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, pp. 1609-1615 (1991). One such stable bis-nitrile oxide, 2,4,6-triethylbenzene-1,3-bis(nitrile oxide), has been shown to be useful for the vulcanization of natural rubber.

None of the above-cited art suggests the use of stable polynitrile oxides as curatives for latexes. It would be an advance in the art to cure latexes using a one-part, room-temperature curative.

The present invention is a water-insoluble aqueous dispersion comprising a stable polynitrile oxide represented by the structure:



where x is an integer greater than 1, G is an aromatic, aliphatic, or cycloaliphatic group having at least one substituent adjacent to each nitrile oxide group, the substituent characterized by inhibiting dimerization of nitrile oxide, and being non-interfering with a reaction between nitrile oxide groups and unsaturated groups.

In a second aspect, the present invention is a method of curing a latex having a polyunsaturated disperse phase, comprising the steps of:

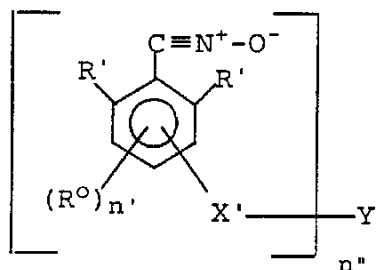
a) mixing with the latex a water-insoluble, stable polynitrile oxide represented by the structure:



where x is an integer greater than 1, preferably an integer from 2 to 6, G is an aromatic, aliphatic, or cycloaliphatic group having at least one substituent adjacent to each nitrile oxide group, the substituent characterized by inhibiting dimerization of nitrile oxide, and being non-interfering with a reaction between nitrile oxide groups and unsaturated groups; and

b) removing water from the mixture, preferably by evaporation.

In a further aspect, the present invention is a compound having the structure:



wherein each R' is independently C<sub>1</sub>-C<sub>12</sub>-alkyl, F, Cl, Br, I, O-C<sub>1</sub>-C<sub>12</sub>-alkyl, or S-C<sub>1</sub>-C<sub>12</sub>-alkyl; each R<sup>0</sup> is a substituent that does not spontaneously react with the nitrile oxide group; each n' is independently 0, 1, or 2; n'' is an integer greater than 1; each X' is independently a bond or a connecting group; and Y' is a polyvalent radical containing an ether, ester, amide, amine, carbonate, ketone, urethane, arylene, or thioether moiety; or each X' and Y' together are a bond connecting the benzene rings.

The present invention provides a simple means of preparing one-part coating systems that can be cured at room temperature without the release of by-products.

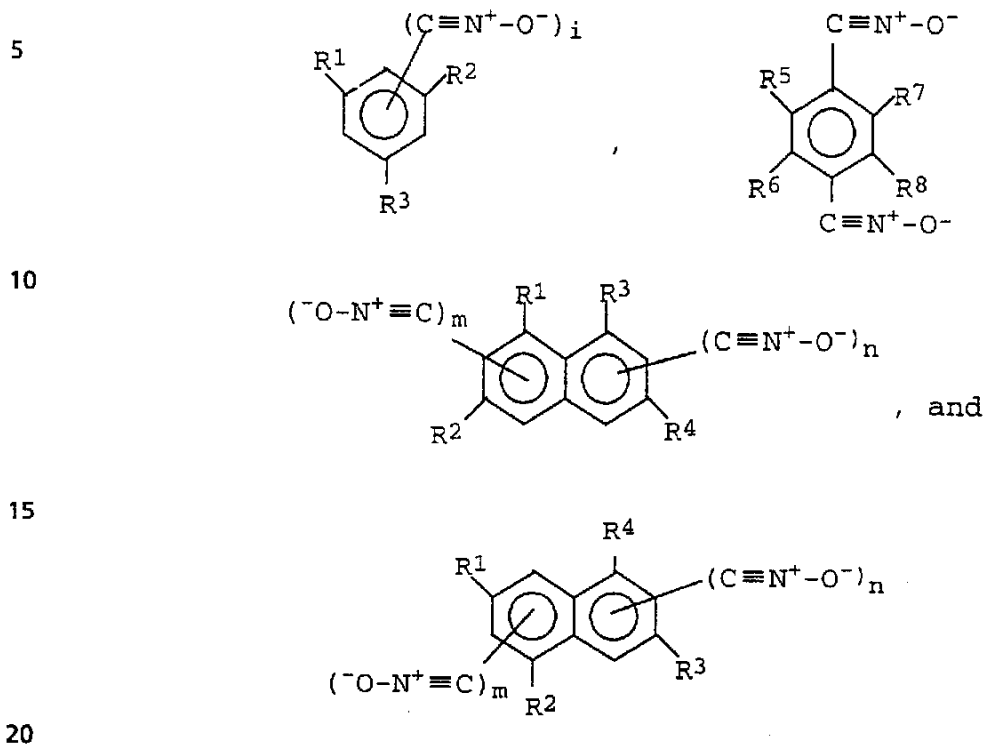
The polynitrile oxides suitable for the practice of the present invention are hindered polynitrile oxides. The term "polynitrile oxide" is used herein to refer to two or more aromatic nitrile oxide groups per molecule. It is to be understood that the term "aromatic" includes heteroaromatic moieties such as pyridines, furans and thiophenes. The term "unsaturated" is used herein to denote a site of the type A=A', or A≡A', where A is a carbon atom, and A' is a carbon, oxygen, nitrogen, sulfur, or phosphorus atom. For the purposes of this invention, a nitrile oxide group is not an unsaturated group. The term "polyunsaturated" is used herein to denote more than one unsaturated group. The preferred unsaturated groups include olefins and alkynes.

Each nitrile oxide is adjacent to at least one substituent that is 1) unreactive with nitrile oxide and 2) non-interfering with the reaction between the nitrile oxide groups and unsaturated groups, preferably olefinically or acetylenically unsaturated groups.

Traditionally, nitrile oxides are prepared in situ in the presence of an unsaturated substrate with which the nitrile oxides are intended to react. However, the stable polynitrile oxide used as a curing agent in the present invention can be prepared separately and is sufficiently stable in the absence of the reactive substrate to be effective as a curing agent.

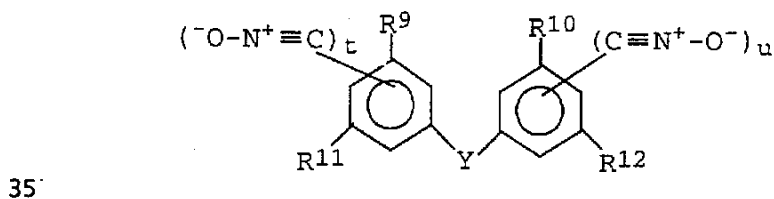
Preferably, the stable polynitrile oxide forms less than 10 percent, more preferably less than 5 percent, and most preferably less than 1 percent dimers in 30 days at room temperature.

Examples of hindered aromatic polynitrile oxides include:

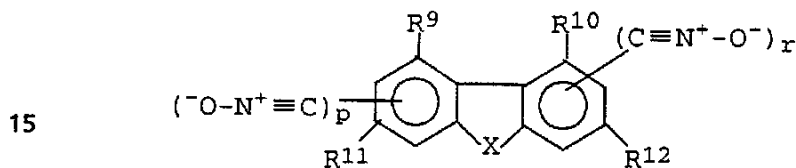
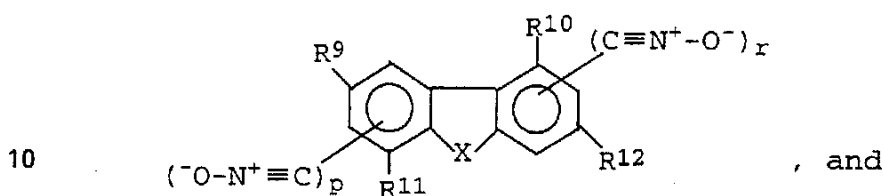
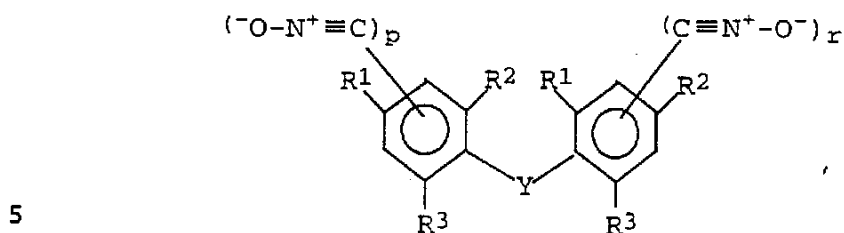


where R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup>, and R<sup>4</sup> are each independently H, R, halo, SH, SR, SOR, SO<sub>2</sub>R, hydroxy, or OR, with the proviso that at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> that is adjacent to a nitrile oxide group is not H; R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, and R<sup>8</sup> are each independently H, R, halo, S-H, SR, SOR, SO<sub>2</sub>R, hydroxy, or OR, wherein R is a C<sub>1</sub>-C<sub>12</sub> linear, branched, or cyclic alkyl group, preferably a C<sub>1</sub>-C<sub>4</sub> linear or branched alkyl group, more preferably ethyl or methyl; or R<sup>5</sup> and R<sup>6</sup>, or R<sup>7</sup> and R<sup>8</sup>, together with the carbon atoms to which they are attached, form a benzene ring, wherein at least one of R<sup>5</sup> or R<sup>7</sup> is not H, and at least one of R<sup>6</sup> or R<sup>8</sup> is not H; i is 2 or 3; m and n are each 0, 1, or 2, and n + m ≥ 2, preferably 2 or 3.

Other examples of hindered aromatic polynitrile oxides include compounds represented by the following structures:

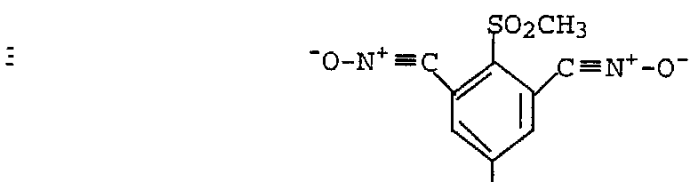
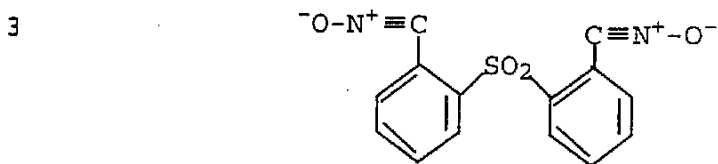
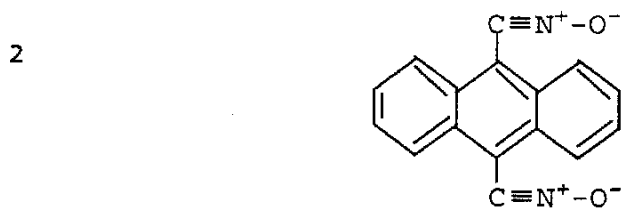


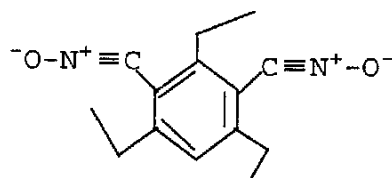
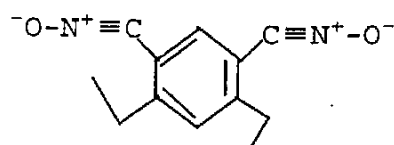
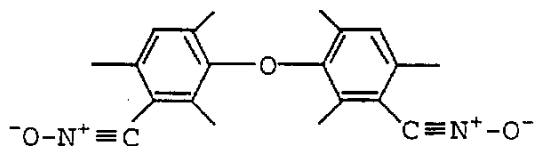
where R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, and R<sup>12</sup> are each independently H, R, halo, SH, SR, SOR, SO<sub>2</sub>R, hydroxy, or OR with the proviso that at least one of R<sup>9</sup> and R<sup>11</sup> is not H when a nitrile oxide group is adjacent to



both  $R^9$  and  $R^{11}$ , and at least one of  $R^{10}$  and  $R^{12}$  is not H when a nitrile oxide group is adjacent to both  $R^{10}$  and  $R^{12}$ ; m, p, and r are each 0, 1, or 2, and  $p + r \geq 2$ ; X is  $\text{CH}_2$ ,  $\text{C}(\text{R})_2$ , carbonyl, O, S, SO,  $\text{SO}_2$ , NH,  $\text{SO}_2\text{NH}$ ,  $\text{SO}_2\text{NR}$ , or NR; t and u are each 0, 1, 2, or 3; and  $t + u \geq 2$ ; Y is a bond,  $\text{CH}_2$ ,  $\text{C}(\text{R})_2$ , carbonyl, O, S, SO,  $\text{SO}_2$ , NH, NR, 9,9'-fluoreno, or phenylene.

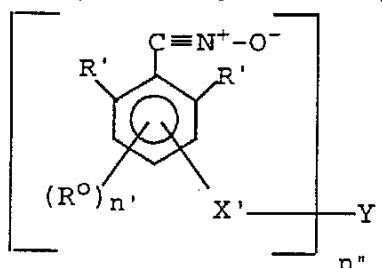
Examples of specific hindered aromatic polynitrile oxides that are suitable for the practice of the present invention include the following compounds:





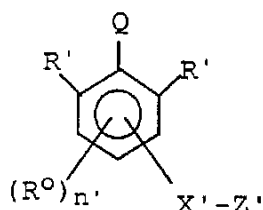
Stable aliphatic or cycloaliphatic polynitrile oxides can be prepared from a suitably functionalized aliphatic or cycloaliphatic polyaldehyde. The polyaldehyde can then be reacted with hydroxylamine to form the polyaldoxime, which can then be treated with bleach and caustic treatment to form the desired aliphatic polynitrile oxide.

A suitably functionalized aromatic mononitrile oxide or monoaldehyde can be used to prepare a polynitrile oxide represented by the following formula:



wherein each  $R'$  is independently  $C_1$ - $C_{12}$ -alkyl, F, Cl, Br, I,  $O$ - $C_1$ - $C_{12}$ -alkyl, or  $S$ - $C_1$ - $C_{12}$ -alkyl; more preferably ethyl, methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, methoxy, ethoxy; most preferably ethyl, methyl, or methoxy; each  $R^O$  is a substituent that does not spontaneously react with the nitrile oxide group, preferably ethyl, methyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, methoxy, ethoxy, F, Cl, Br, or I; each  $n'$  is independently 0, 1, or 2;  $n'$  is an integer greater than 1, preferably 2, 3, or 4, more preferably 2 or 3, and most preferably 2; each  $X'$  is independently a bond or a connecting group such as an alkylene, cycloalkylene, or arylene group, more preferably a bond, a methylene group, or a phenylene group; and  $Y'$  is a polyvalent radical, preferably a divalent radical, containing an ether, ester, amide, carbonate, ketone, urethane, arylene, or thioether group; or each  $X'$  and  $Y'$  together are a bond connecting the benzene rings.

Suitably functionalized hindered aromatic mononitrile oxides or monoaldehydes preferably include 2,6-disubstituted benzonitrile oxides or benzaldehydes having an ester, acetate, hydroxy, epoxy, fluorine, chlorine, bromine, or iodine group connected directly to the benzene ring or indirectly through a connecting group. Preferably, the suitably functionalized 2,6-disubstituted benzonitrile oxide or benzaldehydes is represented by the following structure:

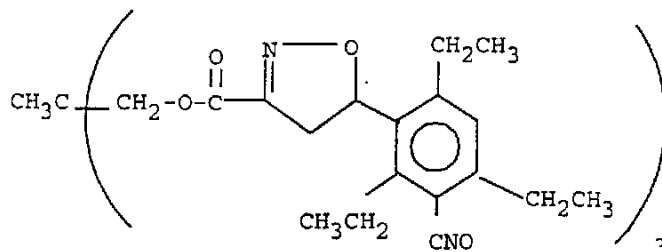


where R', R°, X', and n' are previously defined; Q is  $-C\equiv N^+O^-$  or  $-CHO$ ; and Z' is an ester, acetate, amine, hydroxy, epoxy, amide, keto, aldehyde, fluorine, chlorine, bromine, or iodine group.

For example, 3-hydroxymethyl-2,4,6-trimethylbenzonitrile oxide or its corresponding benzaldehyde precursor can be: (a) transesterified with a diester or condensed with a diacid chloride to form a dinitrile oxide diester; (b) reacted with phosgene to form a dinitrile oxide containing a carbonate group; (c) reacted with a diisocyanate to form a dinitrile oxide containing urethane groups; (d) reacted with a dibenzyl chloride to form a dinitrile oxide containing two ether groups; (e) reacted with a diglycidyl ether to form a dinitrile oxide containing ether groups and hydroxy groups reacted with an acid to form a dinitrile oxido dibenzyl ether.

Similarly, the suitably functionalized hindered aromatic nitrile oxide can be reacted with a second suitably functionalized hindered aromatic nitrile oxide to form a dinitrile oxide. For example, 3-hydroxymethyl-2,4,6-trimethylbenzonitrile oxide can be reacted with 3-chloromethyl-2,6-dimethylbenzene nitrile oxide to form a bis(nitrile oxide) dimethyl ether.

Polynitrile oxides having a functionality of greater than 2 (for example, a trinitrile oxide) can readily be prepared by reacting a dinitrile oxide with a compound having more than 2 unsaturated sites. For example, 2,4,6-triethylbenzene-1,3-dinitrile oxide can be reacted with trimethylol propane triacrylate to form the following trinitrile oxide:

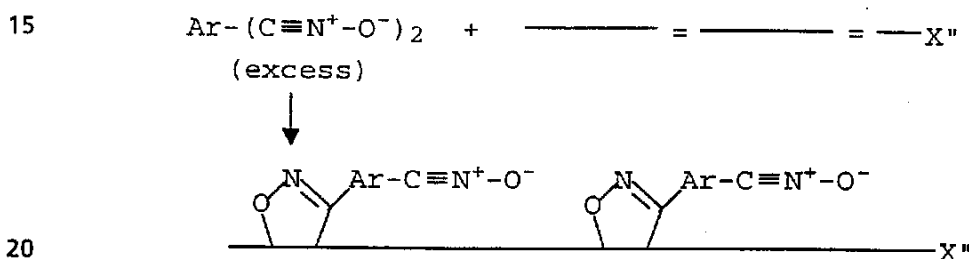




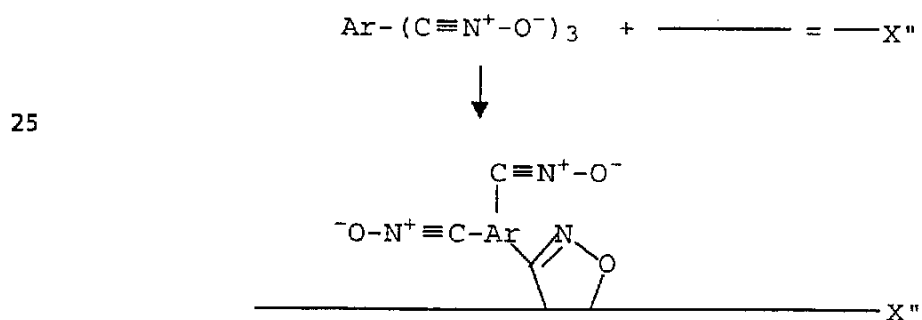
An aqueous dispersion of the stable polynitrile oxide is prepared, then advantageously combined with an aqueous dispersion of a polyunsaturated monomer or polymer or a combination thereof, to make a stable multicomponent dispersion. The term "stable multicomponent dispersion" is used herein to mean that microscopic mixing (and therefore, the reaction rate) of the polynitrile oxide and the polyunsaturated monomer and/or polymer is slower than it would be in the absence of the aqueous medium. Preferably, the extent of the reaction between the polynitrile oxide and polyunsaturated monomer and/or polymer dispersions is less than 10 percent in 8 hours, more preferably less than 10 percent in 30 days, and most preferably less than 10 percent in 1 year.

The aqueous dispersion of the polynitrile oxide can be prepared by emulsifying an emulsifiable concentrate of the polynitrile oxide. This concentrate can be prepared, for example, by mixing a solution of the polynitrile oxide with a surfactant.

The polynitrile oxide may itself be prepared as a surfactant, for example, by reacting an excess of a dinitrile oxide with a polyunsaturated surfactant:



or, for example, by reacting a trinitrile oxide with a monounsaturated surfactant:



where X'' is a hydrophilic group, such as a poly(oxyethylene), a carboxylate, or a sulfate.

Other methods of forming a polynitrile oxide surfactant include reacting the polynitrile oxide with a polymeric surfactant having polyunsaturation:

